Volume 18 | Number 36 | 28 September 2016 | Pages 24759–25766

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PAPER

W. Kunz, M. Kellermeier *et al.*

Diffusion and precipitation processes in iron-based silica gardens

175 YEARS

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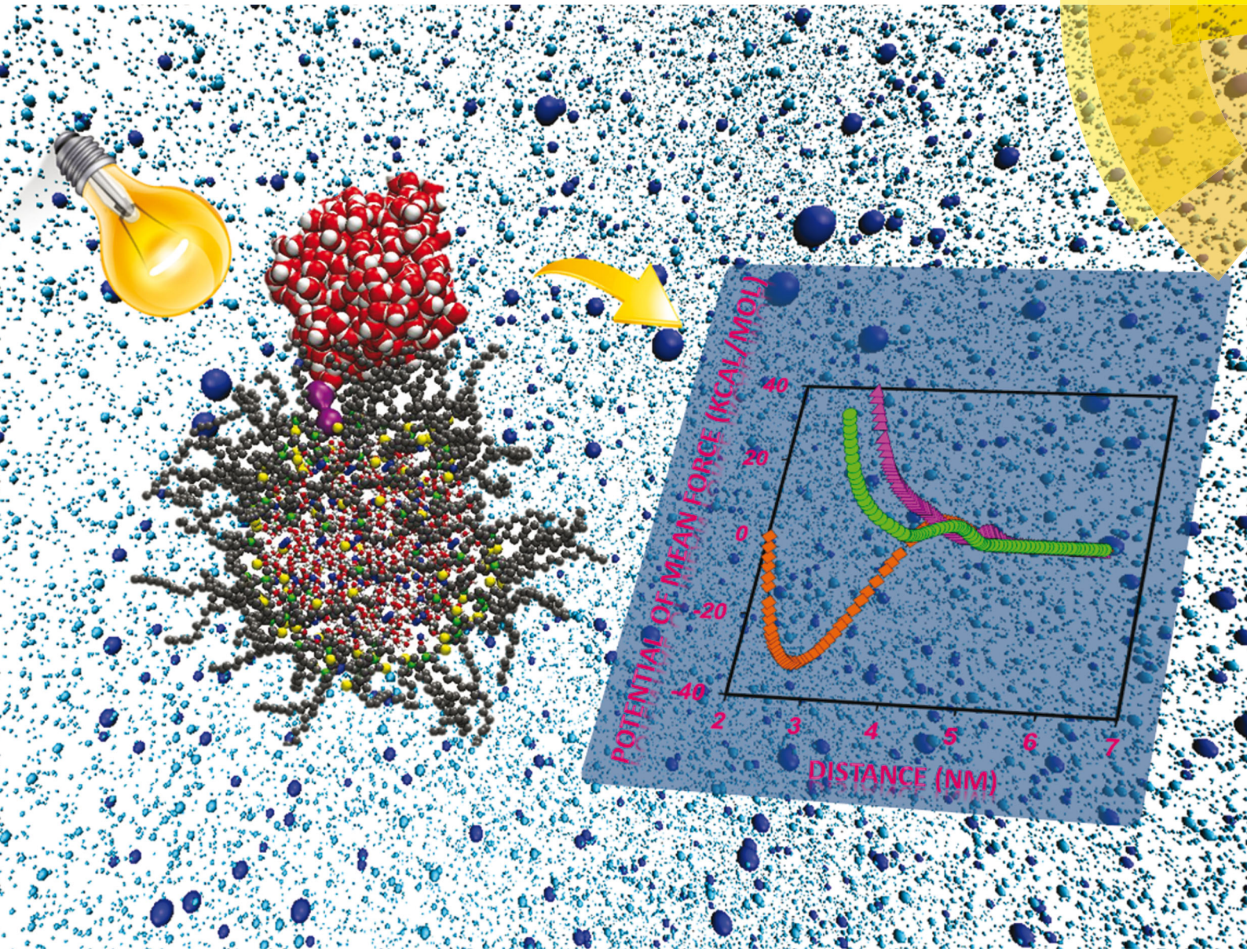

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Alberto Striolo *et al.*

Molecular mechanisms responsible for hydrate anti-agglomerant performance

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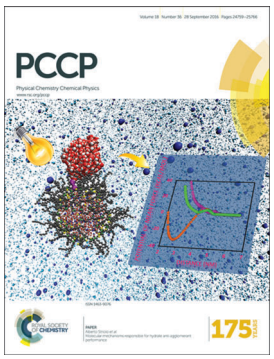
IN THIS ISSUE

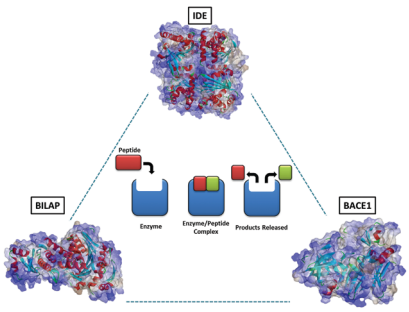
ISSN 1463–9076 CODEN PPCPFQ 18(36) 24759–25766 (2016)

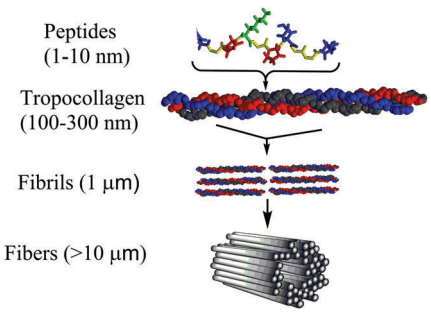
Cover
See W. Kunz, M. Kellermeier *et al.*, pp. 24850–24858. Image reproduced by permission of M. Kellermeier from *Phys. Chem. Chem. Phys.*, 2016, **18**, 24850.



Inside cover
See Alberto Striolo *et al.*, pp. 24859–24871. Image reproduced by permission of Alberto Striolo from *Phys. Chem. Chem. Phys.*, 2016, **18**, 24859.

PERSPECTIVES





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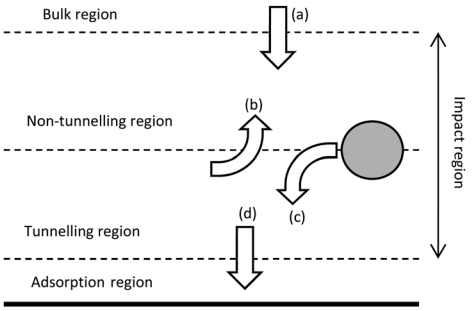
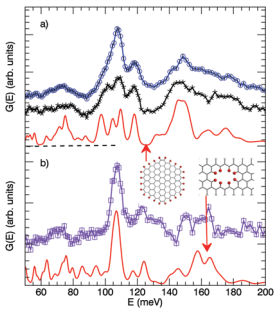
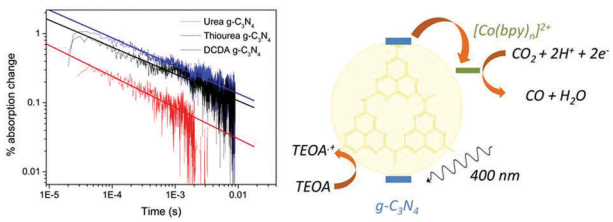
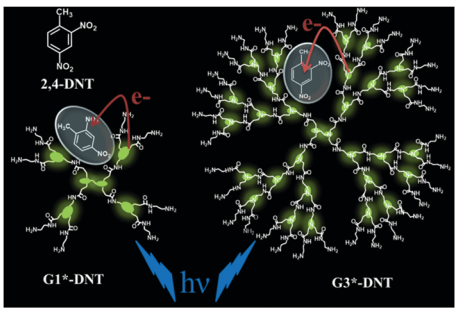


COMMUNICATIONS







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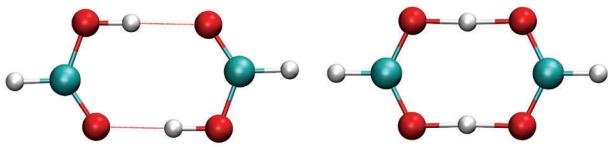
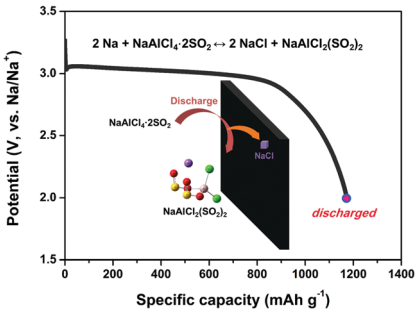


An *ab initio* potential energy surface for the formic acid dimer: zero-point energy, selected anharmonic fundamental energies, and ground-state tunneling splitting calculated in relaxed 1–4-mode subspaces

Chen Qu and Joel M. Bowman*

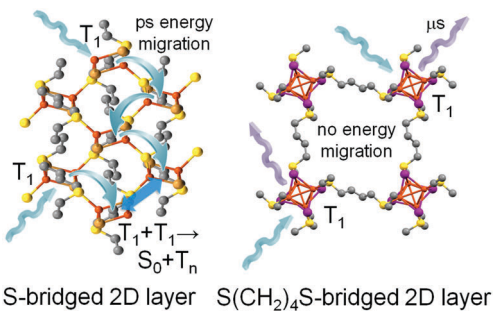
We report a full-dimensional, permutationally invariant potential energy surface (PES) for the cyclic formic acid dimer.



A joint experimental and theoretical determination of the structure of discharge products in Na–SO_2 batteries

Young-Kyu Han,* Goojin Jeong, Keon-Joon Lee, Taeeun Yim* and Young-Jun Kim*

This work is the first to elucidate the governing mechanism of molten-salt batteries by combining experimental and theoretical NMR measurements.

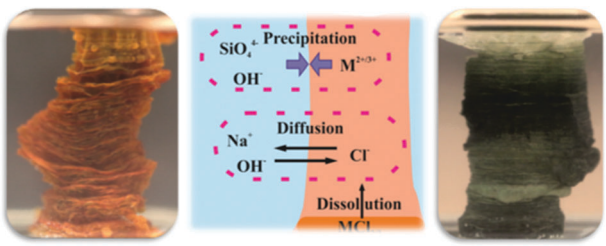


The 3D $[(Cu_2Br_2)\{\mu\text{-}EtS(CH_2)_4SEt\}]_n$ material: a rare example of a coordination polymer exhibiting triplet–triplet annihilation

Antoine Bonnot, Paul-Ludovic Karsenti, Frank Juvenal, Christopher Golz, Carsten Strohmann, Daniel Fortin, Michael Knorr* and Pierre D. Harvey*

A very rare case of excitation energy migration has been observed for an inorganic material.

RESEARCH PAPERS



Diffusion and precipitation processes in iron-based silica gardens

F. Glaab, J. Rieder, J. M. García-Ruiz, W. Kunz* and M. Kellermeier*

The time-dependent dynamic evolution of macroscopic silica garden tubes is shown to strongly depend on the used metal cations.

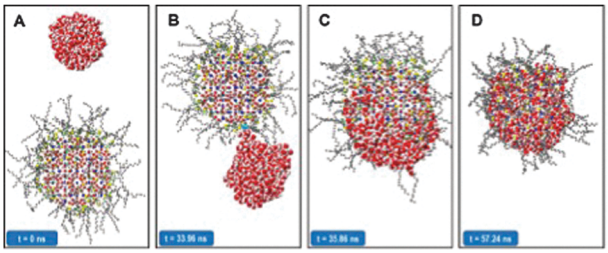
RESEARCH PAPERS

24859

Molecular mechanisms responsible for hydrate anti-agglomerant performance

Anh Phan, Tai Bui, Erick Acosta, Pushkala Krishnamurthy and Alberto Striolo*

Steered and equilibrium molecular dynamics simulations were employed to study the coalescence of a sI hydrate particle and a water droplet within a hydrocarbon mixture.

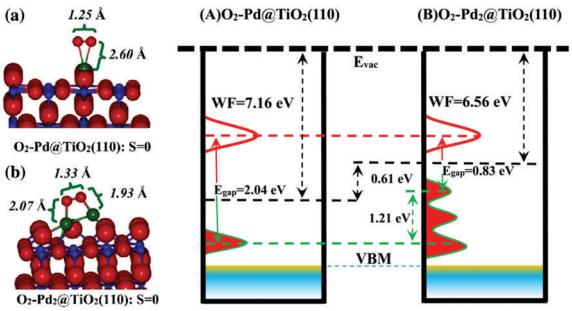


24872

Interplay between the spin-selection rule and frontier orbital theory in O_2 activation and CO oxidation by single-atom-sized catalysts on TiO_2(110)

Shunfang Li, Xingju Zhao, Jinlei Shi, Yu Jia, Zhengxiao Guo, Jun-Hyung Cho,* Yanfei Gao and Zhenyu Zhang*

Distinct chemical activities of a Pd monomer and a Pd_2 dimer supported on TiO_2(110) for O_2 activation.

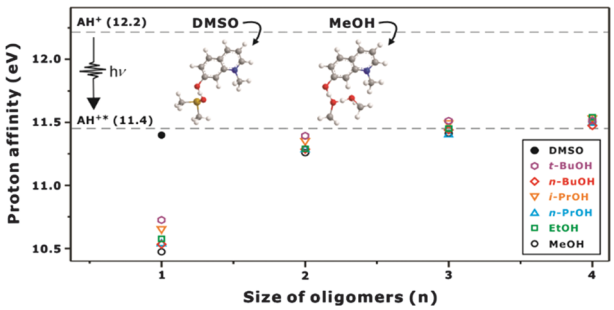


24880

The critical size of hydrogen-bonded alcohol clusters as effective Brønsted bases in solutions

Sun-Young Park, Taeg Gyum Kim, Manjaly J. Ajitha, Kijeong Kwac, Young Min Lee, Heesu Kim, Yousung Jung* and Oh-Hoon Kwon*

Hydrogen-bonded clustering of alcohol molecules increases their basicity (proton affinity) significantly, so that alcohol dimers can accept a proton which otherwise is impossible due to insufficient basicity as a monomer.

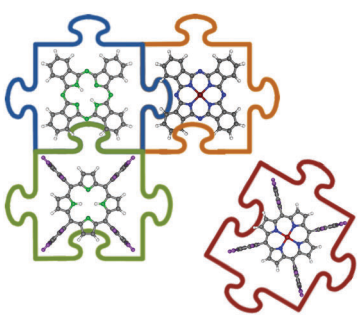


24890

Electronic structure of CuTPP and CuTPP(F) complexes: a combined experimental and theoretical study II

Giulia Mangione, Mauro Sambi, Silvia Carlotto, Andrea Vittadini, Giovanni Ligorio, Melanie Timpel, Luca Pasquali, Angelo Giglia, Marco Vittorio Nardi and Maurizio Casarin*

CuTPP and CuTPP(F) thick films deposited on Au(111) have been studied by coupling NEXAFS spectroscopy at the $^{C/N/F}$K-edges and $^{Cu}L_{2,3}$-edges and spin-unrestricted TD-DFT calculations.



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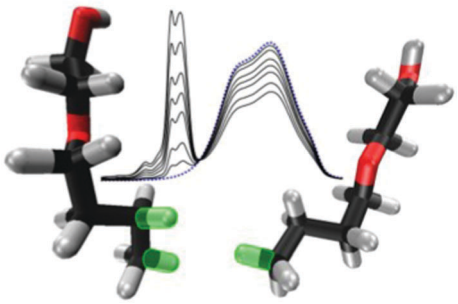

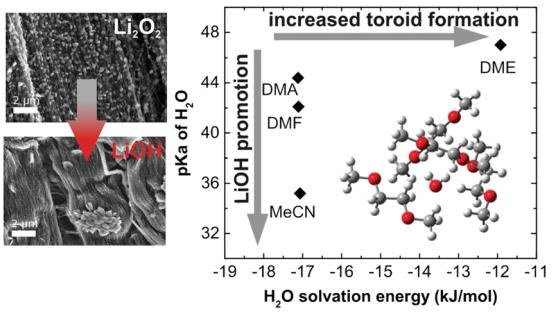

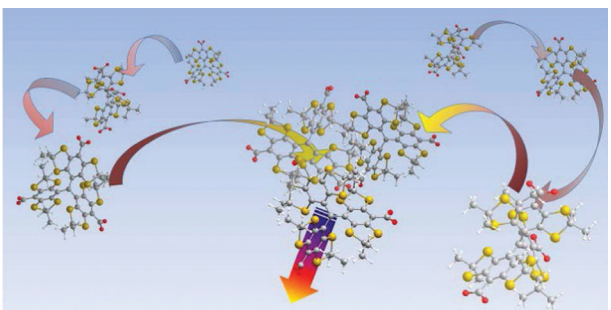

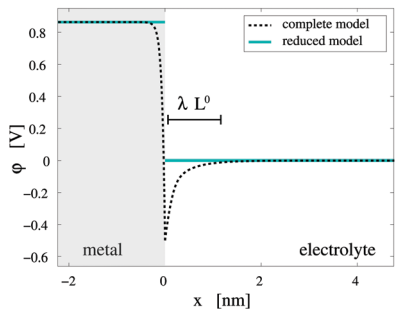

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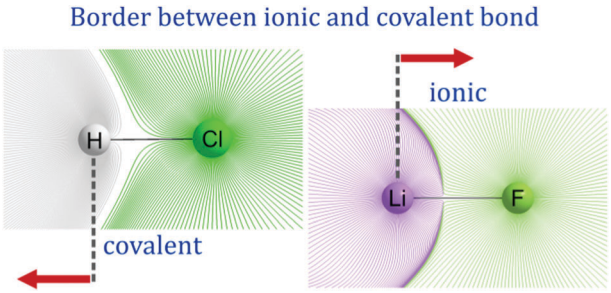

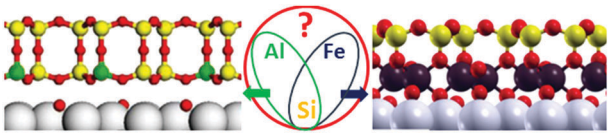

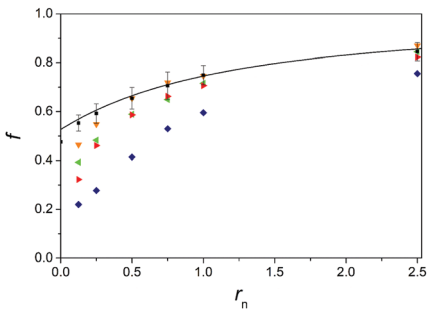

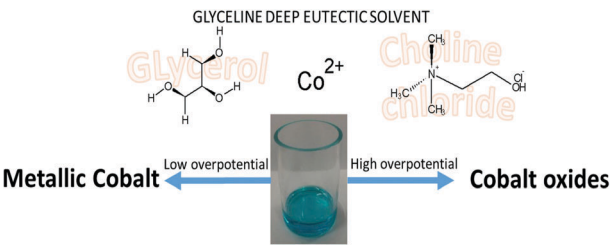

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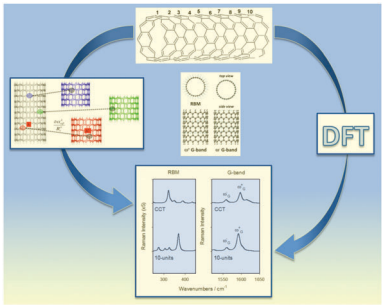
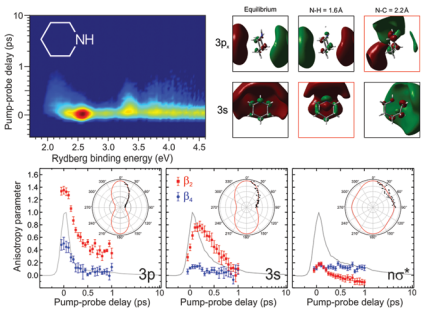


Calculation of Raman parameters of real-size zigzag (*n*, 0) single-walled carbon nanotubes using finite-size models

Teobald Kupka,* Michal Stachów, Leszek Stobiński and Jakub Kaminský*

Structural and selected Raman features of real-size single-walled carbon nanotubes (SWCNTs) were studied using finite-size pristine SWCNT models at the DFT level.

25070

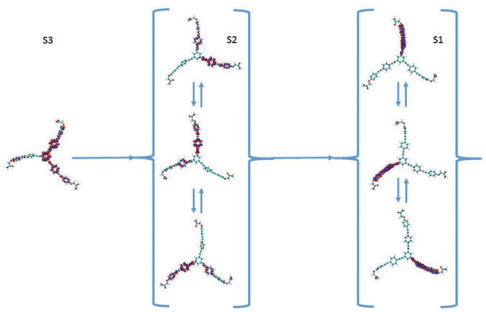


Ultrafast relaxation dynamics of electronically excited piperidine: ionization signatures of Rydberg/valence evolution

Liv B. Klein, James O. F. Thompson, Stuart W. Crane, Lisa Saalbach, Theis I. Sølling, Martin J. Paterson and Dave Townsend*

Time-resolved photoelectron spectroscopy reveals distinct ionization signatures of Rydberg-to-valence state evolution in the secondary aliphatic amine piperidine.

25080

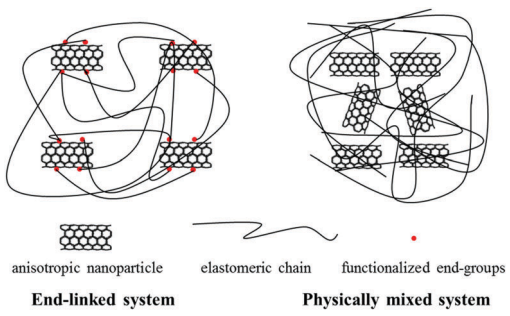


Ultrafast electronic energy relaxation in a conjugated dendrimer leading to inter-branch energy redistribution

D. Ondarse-Alvarez, S. Kömürlü, A. E. Roitberg, G. Pierdominici-Sottile, S. Tretiak, S. Fernandez-Alberti* and V. D. Kleiman*

Dendrimers are arrays of coupled chromophores, where the energy of each unit depends on its structure and conformation.

25090



Tuning the structure and mechanical property of polymer nanocomposites by employing anisotropic nanoparticles as netpoints

Zijian Zheng, Fanzhu Li, Hongji Liu, Jianxiang Shen, Jun Liu,* Youping Wu,* Liqun Zhang and Wenchuan Wang

We report a new kind of polymer nanocomposite by means of employing anisotropic nanoparticles as netpoints, to chemically connect the dual end-groups of each polymer chain to form a network.

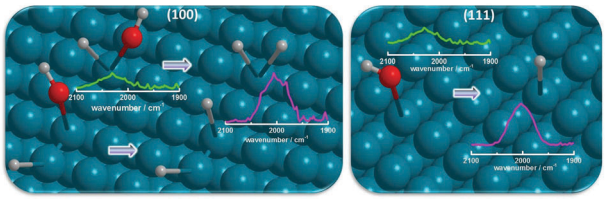
RESEARCH PAPERS

25100

Mechanism of the potential-triggered surface transformation of germanium in acidic medium studied by ATR-IR spectroscopy

Simantini Nayak and Andreas Erbe*

During the electrochemical surface transformation of Ge(100) and Ge(111) surfaces from an –OH to an –H terminated surface, different potential dependent transient species are observed.

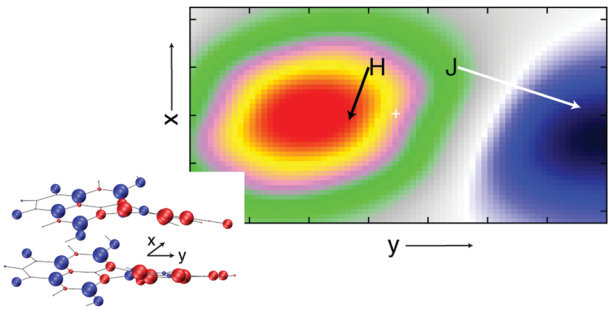


25110

Biphasic aggregation of a perylene bisimide dye identified by exciton-vibrational spectra

P.-A. Plötz, S. P. Polyutov, S. D. Ivanov, F. Fennel, S. Wolter, T. Niehaus, Z. Xie, S. Lochbrunner, F. Würthner and O. Kühn*

The quantum efficiency of light emission supramolecular aggregates strongly depends on the intermolecular coupling. We present a molecule which demonstrates two different aggregated structures with high and low quantum efficiency. The spectral signatures can be understood by simulating the aggregated structures and the corresponding exciton-vibrational spectra.

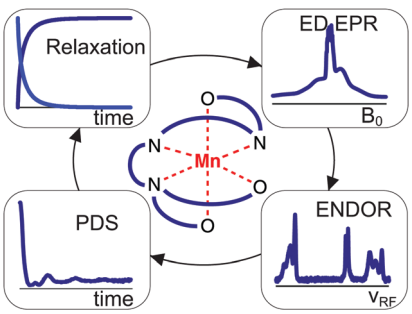


25120

EPR characterization of Mn(II) complexes for distance determination with pulsed dipolar spectroscopy

Katharina Keller, Michal Zalibera, Mian Qi, Vanessa Koch, Julia Wegner, Henrik Hintz, Adelheid Godt,* Gunnar Jeschke, Anton Savitsky* and Maxim Yulikov*

EPR properties of four Mn(II) complexes and Tikhonov regularization-based analysis of RIDME data containing dipolar overtones are presented.

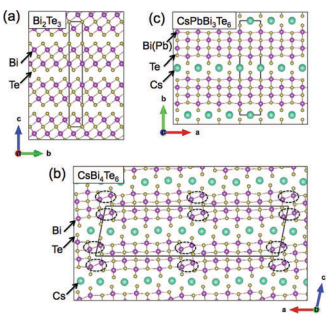


25136

Determination of the local structure of $CsBi_{4-x}Pb_xTe_6$ (x = 0, 0.5) by X-ray absorption spectroscopy

Takanori Wakita,* Eugenio Paris, Takashi Mizokawa, Muammer Yasin Hacisalihoğlu, Kensei Terashima, Hiroyuki Okazaki, Olivier Proux, Isabelle Kieffer, Eric Lahera, William Del Net, Luca Olivi, Yoshihiko Takano, Yuji Muraoka, Takayoshi Yokoya and Naurang L. Saini

We have studied the local structure and valence electronic unoccupied states of $CsBi_4Te_6$ and $CsBi_{3.5}Pb_{0.5}Te_6$ ($T_c \sim 3$ K) by EXAFS and XANES measurements.



RESEARCH PAPERS

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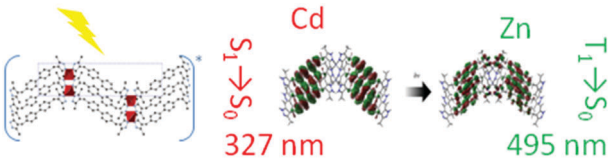

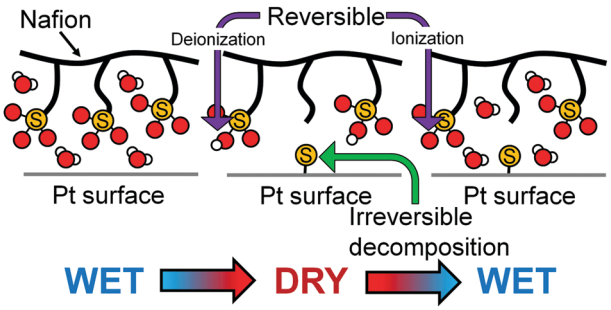

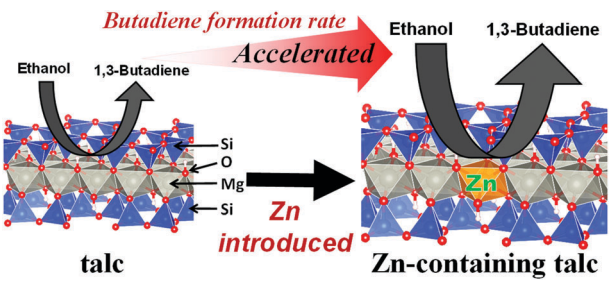

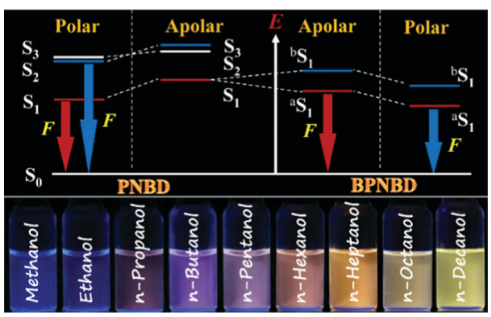

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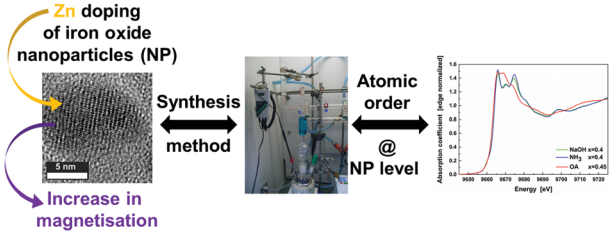
25221

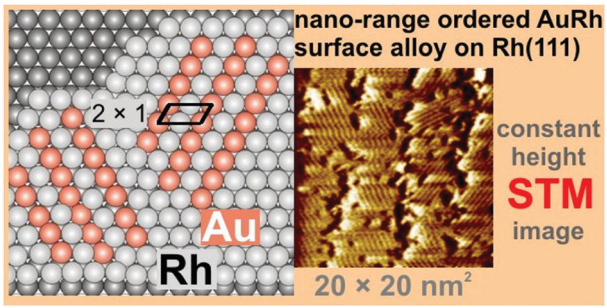


Pushing up the magnetisation values for iron oxide nanoparticles *via* zinc doping: X-ray studies on the particle's sub-nano structure of different synthesis routes

Wojciech Szczerba,* Jan Żukrowski, Marek Przybylski, Marcin Sikora, Olga Safonova, Aleksey Shmeliov, Valeria Nicolosi, Michael Schneider, Tim Granath, Maximilian Oppmann, Marion Straßer and Karl Mandel*

We study how only slightly different synthesis approaches towards zinc doped iron oxide nanoparticles strongly influences the resulting structure and magnetisation.

25230

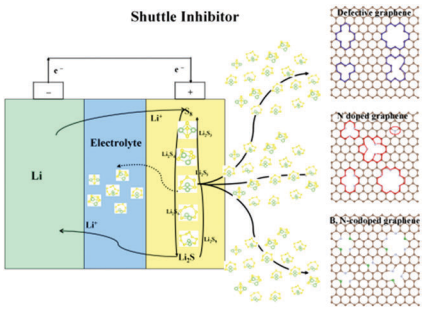


The growth and thermal properties of Au deposited on Rh(111): formation of an ordered surface alloy

László Óvári,* András Berkó,* Gábor Vári, Richárd Gubó, Arnold Péter Farkas and Zoltán Kónya

Scanning tunnelling microscopy (STM), low energy ion scattering spectroscopy (LEIS), X-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS) were applied for studying Au deposited on the Rh(111) surface.

25241

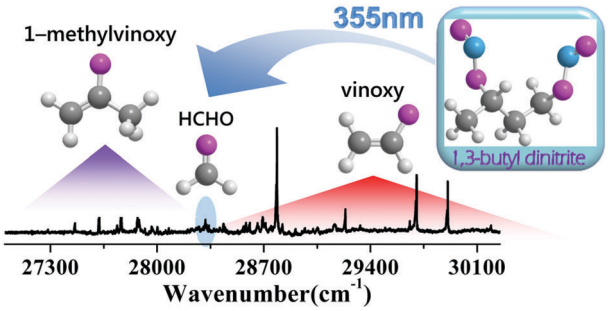


Shuttle inhibition by chemical adsorption of lithium polysulfides in B and N co-doped graphene for Li–S batteries

Fen Li, Yan Su and Jijun Zhao*

The shuttle effect can be effectively depressed by the synergistic contribution of N···Li and B···S interactions.

25249



Photodissociation dynamics of dinitrite at 355 nm: initiation of a reactive pathway

Lingxuan Wang and Lily Zu*

Vinoxy and 1-methylvinoxy radicals were detected along with formaldehyde as the products in the photodissociation of 1,3-butyl dinitrite.

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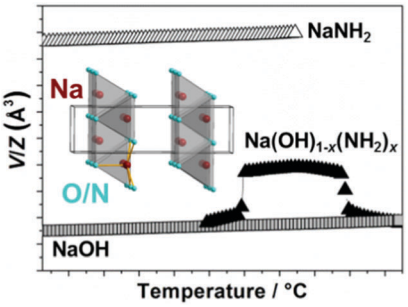

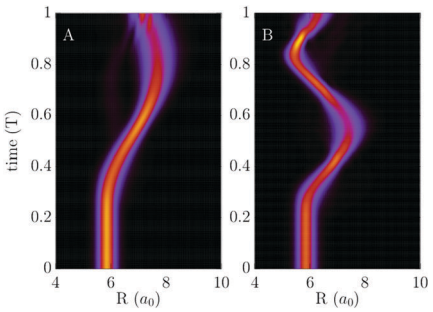

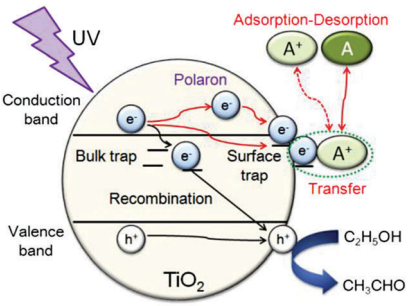

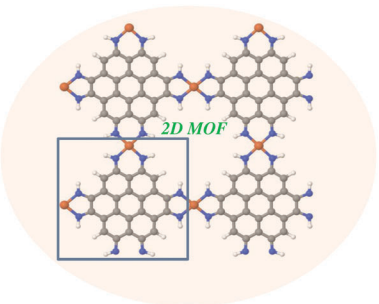

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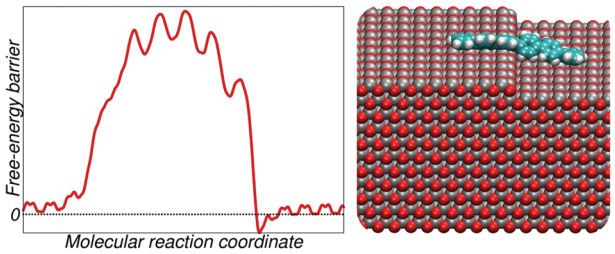

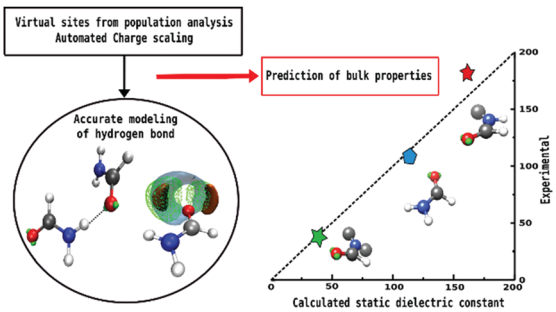

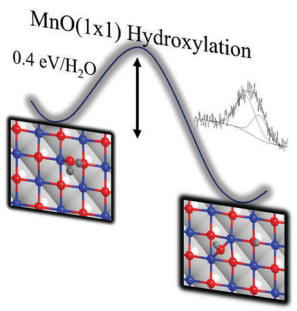

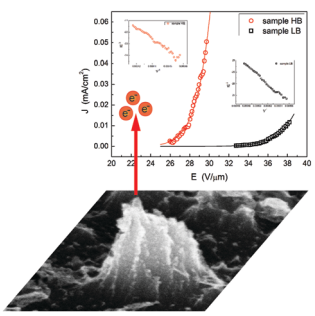

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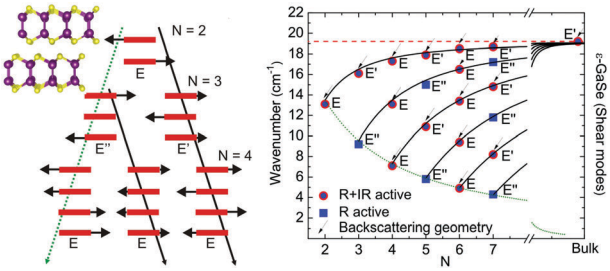
25401

Ultra-weak interlayer coupling in two-dimensional gallium selenide

R. Longuinhos and J. Ribeiro-Soares*

By using symmetry arguments and first principles calculations, we study the stability of β and ε few-layer GaSe and their low-frequency interlayer breathing and shear modes, unveiling uncommon lubricant properties and exfoliability at the nanoscale.

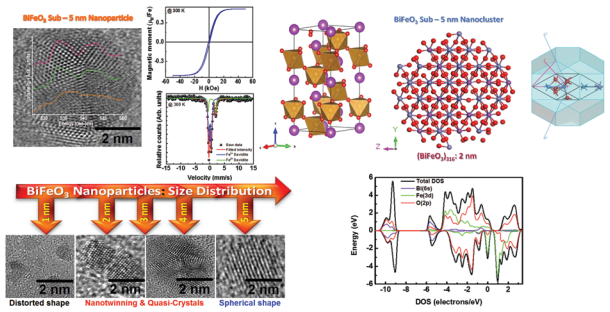


25409

Observation of nanotwinning and room temperature ferromagnetism in sub-5 nm $BiFeO_3$ nanoparticles: a combined experimental and theoretical study

Mandar M. Shirolkar,* Xiaolei Dong, Jieni Li, Shiliu Yin, Ming Li and Haiqian Wang*

The nanotwinning, covalent nature and magnetic properties of $BiFeO_3$ nanoparticles of sub-5 nm size are investigated.

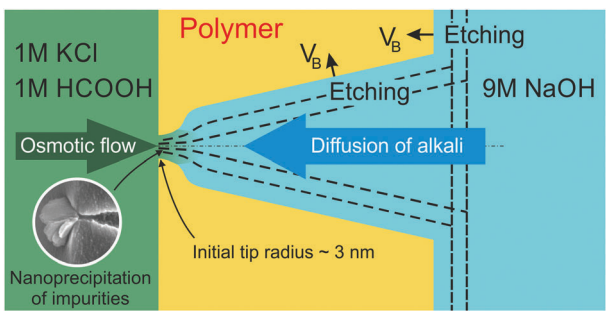


25421

Shedding light on the mechanism of asymmetric track etching: an interplay between latent track structure, etchant diffusion and osmotic flow

Pavel Y. Apel,* Valery V. Bashevoy, Irina V. Blonskaya, Nikolay E. Lizunov, Oleg L. Orelovitch and Christina Trautmann

Asymmetric etching of ion tracks is strongly affected by osmotic flow which has a determinative effect on nanopore geometry. As a result, the narrowest part of the pore evolves through a variety of configurations.

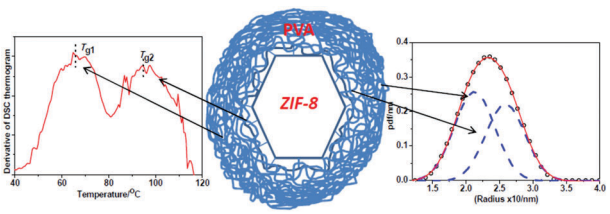


25434

Unraveling the sub-nanoscopic structure at interphase in a poly(vinyl alcohol)–MOF nanocomposite, and its role in thermo-mechanical properties

S. K. Sharma, K. Sudarshan and P. K. Pujari*

Polymer chain framework at the interfacial region in PVA–MOF nanocomposites can be represented by a rigid but rather open network.



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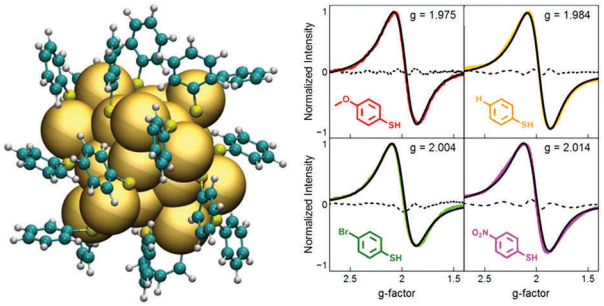
25443

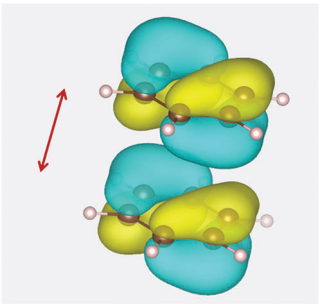


Probing ligand-induced modulation of metallic states in small gold nanoparticles using conduction electron spin resonance

Anthony Cirri, Alexey Silakov, Lasse Jensen and Benjamin J. Lear*

We acquire conduction electron spin resonance spectra for small gold nanoparticles protected by a series of *para*-substituted thiophenol ligands. Our results demonstrate that changes in ligand identity affect the quantum mechanical behavior of electrons within the nanoparticle's metallic core.

25452

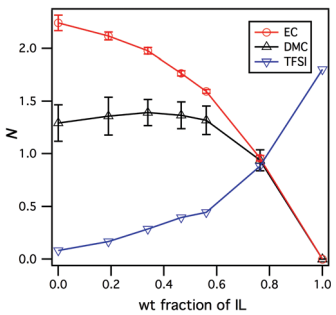


A new insight into π–π stacking involving remarkable orbital interactions

Rundong Zhao and Rui-Qin Zhang*

The importance of orbital interaction in π–π interactions is explored in detail and a unified description of π–π stacking is proposed.

25458

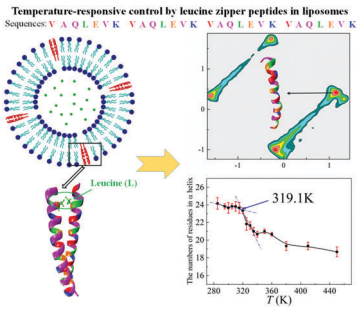


Enhanced low-temperature ionic conductivity *via* different Li^+ solvated clusters in organic solvent/ionic liquid mixed electrolytes

Luis Aguilera, Johan Scheers and Aleksandar Matic*

We investigate Li^+ coordination in mixed electrolytes based on ionic liquids (ILs) and organic solvents and its relation with the macroscopic properties such as phase behaviour and ionic conductivity.

25465



Computational insights into the destabilization of α-helical conformations formed by leucine zipper peptides in response to temperature

Xiejun Xu, Xingqing Xiao, Shouhong Xu and Honglai Liu*

The computed transition temperature of leucine zipper peptides is 319.1 K, which is in quantitative agreement with the experimental measurement, 321.1 K.

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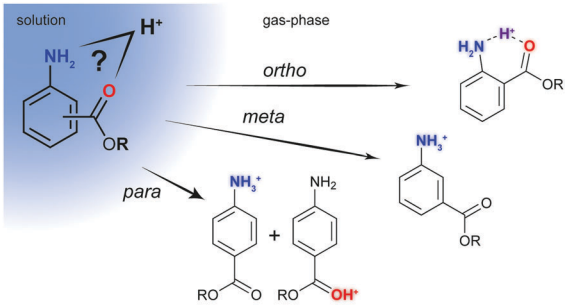

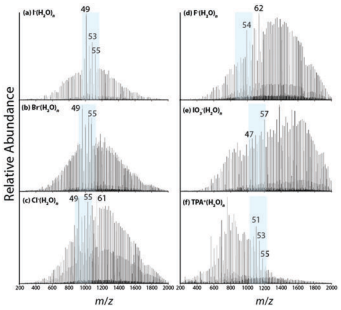

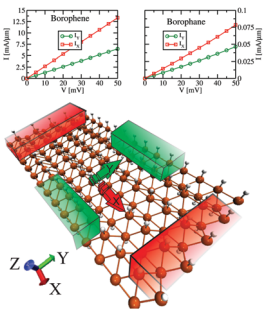

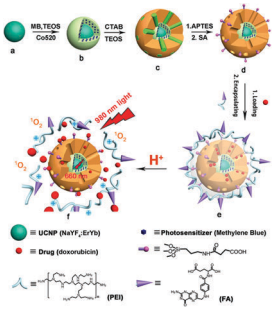

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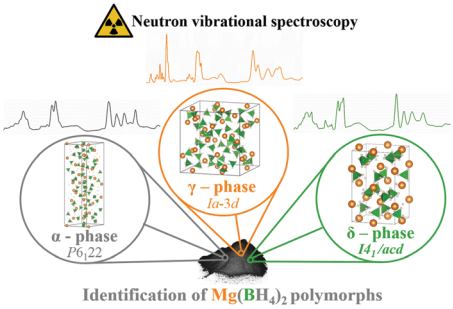

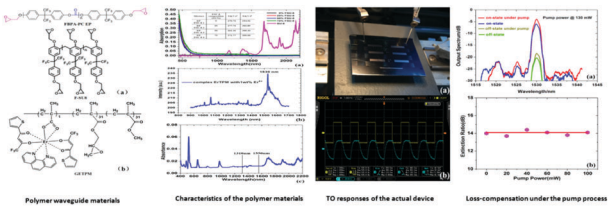

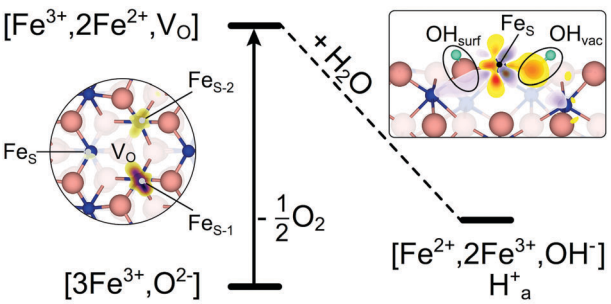

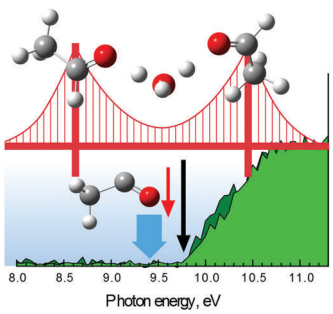

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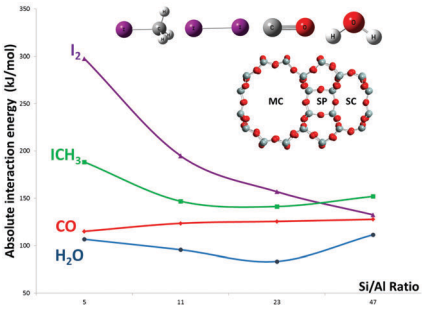
25574

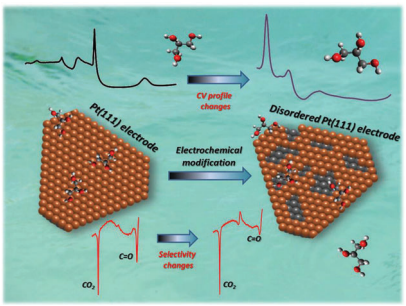


Impact of the Si/Al ratio on the selective capture of iodine compounds in silver-mordenite: a periodic DFT study

Siwar Chibani,* Mouheb Chebbi, Sébastien Lebègue, Laurent Cantrel and Michael Badawi*

Decreasing the Si/Al ratio in silver exchanged mordenite drastically limits the potential inhibiting effect of H_2O and CO on the adsorption of I_2 and ICH_3, and allows a spontaneous dissociation of I_2 leading to the formation of AgI complexes.

25582

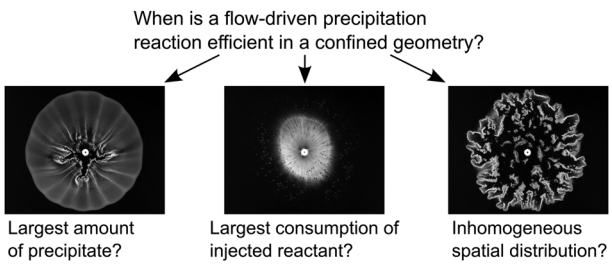


How do random superficial defects influence the electro-oxidation of glycerol on Pt(111) surfaces?

Pablo S. Fernández,* Polina Tereshchuk, Camilo A. Angelucci, Janaina F. Gomes, Amanda C. Garcia, Cauê A. Martins, Giuseppe A. Camara, María E. Martins, Juarez L. F. Da Silva and Germano Tremiliosi-Filho

The glycerol electrooxidation reaction (GEOR) has attracted huge interest in the last decade due to the very low price and availability of this polyol.

25592

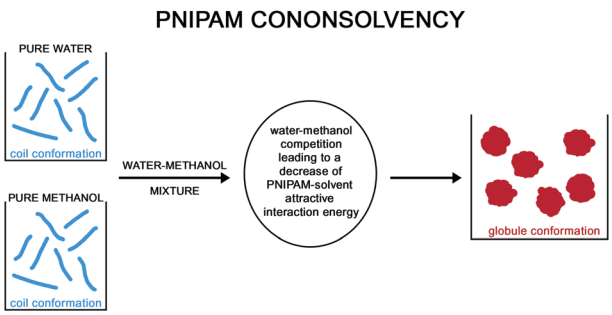


Flow-driven control of calcium carbonate precipitation patterns in a confined geometry

Gábor Schuszter, Fabian Brau and A. De Wit*

Upon injection of an aqueous solution of carbonate into a solution of calcium ions in the confined geometry of a Hele-Shaw cell, various calcium carbonate precipitation patterns are observed.

25601



An alternative explanation of the cononsolvency of poly(*N*-isopropylacrylamide) in water–methanol solutions

Andrea Pica and Giuseppe Graziano*

Water/methanol competition in the interaction with PNIPAM causes a decrease in the magnitude of attractive energy, leading to cononsolvency.

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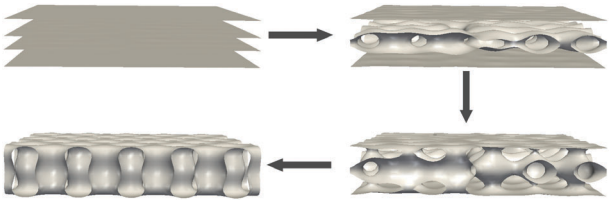

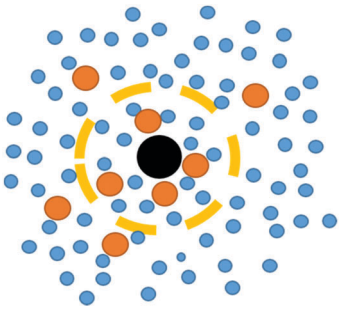

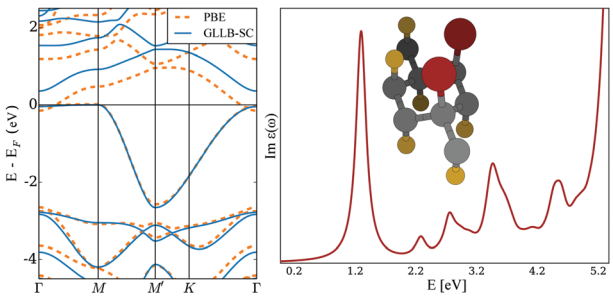

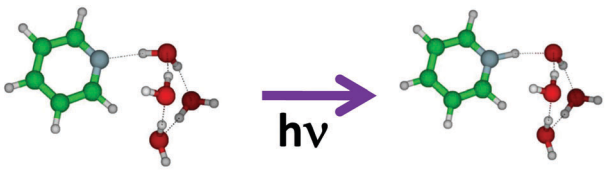

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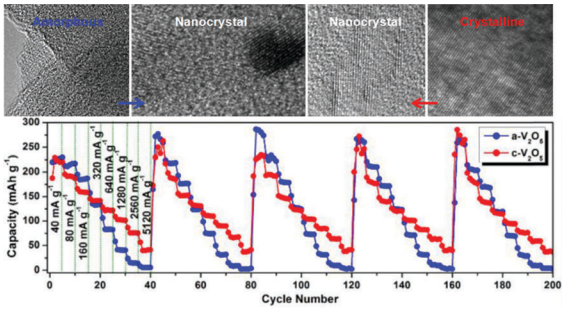
25645

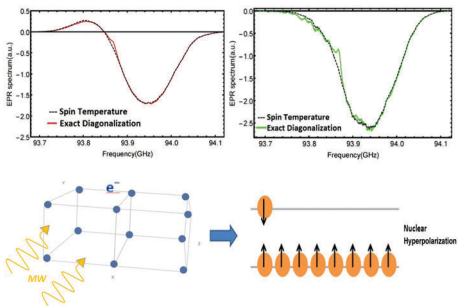


Rational selection of amorphous or crystalline V_2O_5 cathode for sodium-ion batteries

Shikun Liu, Zhongqiu Tong, Jiupeng Zhao,* Xusong Liu, Jing wang, Xiaoxuan Ma, Caixia Chi, Yu Yang, Xiaoxu Liu* and Yao Li*

Amorphous and crystalline V_2O_5 cathodes in sodium ion batteries express inverse capacity values at low and high current densities.

25655

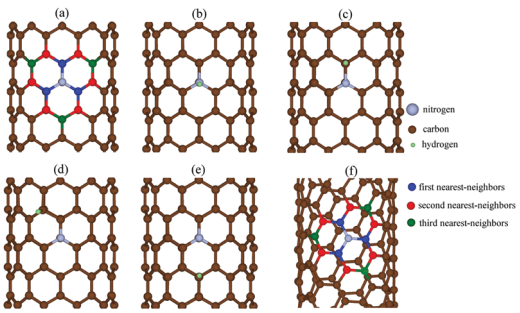


Evidence of spin-temperature in dynamic nuclear polarization: an exact computation of the EPR spectrum

Filippo Caracciolo,* Marta Filibian, Pietro Carretta, Alberto Rosso and Andrea De Luca

We show the validity of the spin-temperature approach for typical radical concentration used in dissolution DNP protocols.

25663

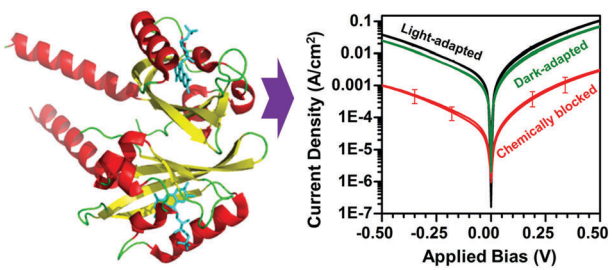


Ab initio study of hydrogen chemisorption in nitrogen-doped carbon nanotubes

Julian David Correa, Elizabeth Florez* and Miguel Eduardo Mora-Ramos

The electronic structure of single walled nitrogen-doped carbon nanotubes is calculated by first principles using density functional theory within the supercell approach with periodic boundary conditions.

25671



Electron transport *via* a soluble photochromic photoreceptor

Sabyasachi Mukhopadhyay, Wolfgang Gärtner, David Cahen,* Israel Pecht* and Mordechai Sheves*

Electron transport properties *via* a photochromic biological photoreceptor have been studied in junctions of monolayer assemblies in solid-state configurations.

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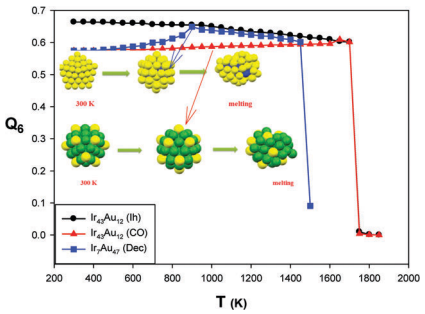
25676

Phase transition in crown-jewel structured Au–Ir nanoalloys with different shapes: a molecular dynamics study

Hamed Akbarzadeh,* Mohsen Abbaspour and Esmat Mehrjouei

We have simulated the melting process for Au–Ir crown-jewel structured in the icosahedral, cuboctahedral, and decahedral morphologies.

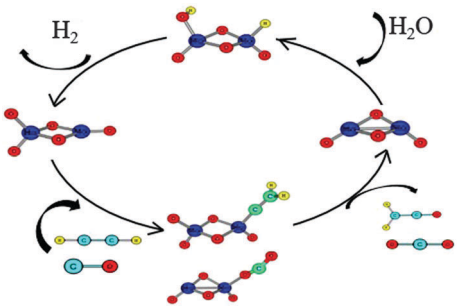


25687

Hydrogen evolution from water using Mo–oxide clusters in the gas phase: DFT modeling of a complete catalytic cycle using a $Mo_2O_4^-/Mo_2O_5^-$ cluster couple

Manisha Ray, Arjun Saha and Krishnan Raghavachari*

Hydrogen evolution from water using sacrificial reagents and Mo–oxide cluster anions has been explored. The internal energy preservation within the clusters plays a key role in the catalytic cycle.

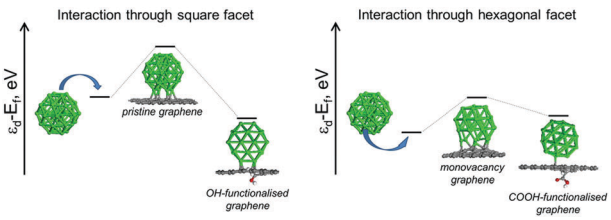


25693

Pt_{38} cluster on OH- and COOH-functionalised graphene as a model for Pt/C-catalysts

M. Matsutsu, M. A. Petersen and E. van Steen*

Shift in d-band centre of facet of Pt_{38}-clusters opposite facet interacting with functionalised graphene indicate effect of support on reactivity.

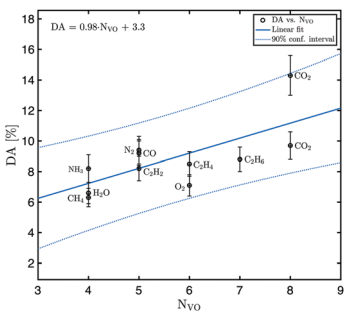


25705

Relative extent of double and single Auger decay in molecules containing C, N and O atoms

A. Hult Roos, J. H. D. Eland, J. Andersson, S. Zagorodskikh, R. Singh, R. J. Squibb and R. Feifel*

We show that the proportion of double Auger decay following creation of single 1s core holes in molecules containing C, N and O atoms is greater than usually assumed, amounting to about 10% of single Auger decay in many cases.



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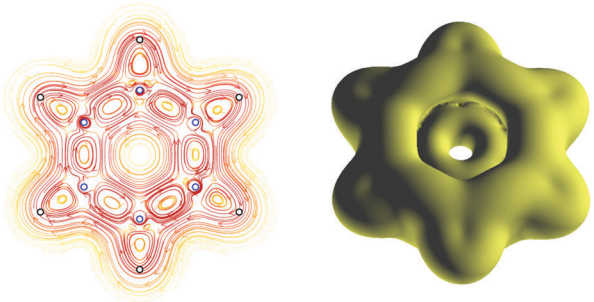

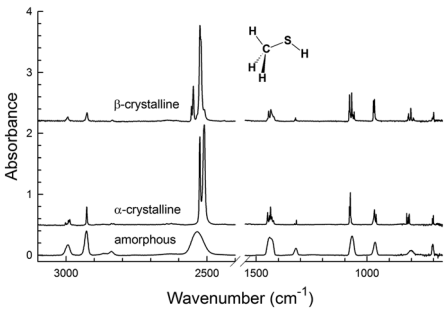

CORRECTION